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BACKGROUND LEVELS OF HYDRAZINE, UDMH, AND NDMA AT TITAN II COMPLEXES DAVIS-MONTHAN AFB, ARIZONA

JULY 1983

USAF Occupational and Environmental Health Laboratory
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This survey evaluated potential exposure levels of hydrazine, UDMH and NDMA during normal Titan II alert operations.

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JULY 1983

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I. INTRODUCTION

A. Background and Purpose:

The USAF Hospital Davis Monthan, Bioenvironmental Engineering Services, Davis-Monthan AFB (USAF Hospital DM/SGPB) performed sampling for hydrazine, unsymmetrical dimethyl hydrazine (UDMH), and nitrosodimethylamine (NDMA) at five active Titan II complexes. These surveys were performed during the period 4 November 1982 through 8 April 1983 at the request of Headquarters Strategic Air Command, Bioenvironmental Engineering Division (HQ SAC/SGPB). The purpose of these surveys was to determine background levels of hydrazine, UDMH and NDMA at typical Titan II complexes in alert status for comparison with results reported during deactivation fuel propellant download operations.

B. USAF Hospital DM/SGPB Survey Personnel:

1. Maj Robert J. Sutay, Certified Industrial Hygienist

2. Capt Arnold R. Ferguson, Bioenvironmental Engineer

3. SSgt James B. Heggie, Bioenvironmental Engineering Technician

II. AIR SAMPLING AND ANALYSIS

A. Sampling and Analysis Techniques

1. Hydrazine/UDMH

Area and personal samples for hydrazine and UDMH were collected using Gas Chrom R^{R} (30/60 mesh) (firebrick) sampling tubes with P200, P200A, P2500, or P2500A DuPont pumps with flow rates ranging from .2 to 2.0 Lpm. Analysis of firebrick tubes was performed by the USAF Occupational and Environmental Health Laboratory, Analytical Services Division (USAF OEHL/SA). After desorption with deionized water, the samples were split and analyzed separately by colorimetric determination for UDMH and hydrazine.

2. NDMA

Area and personal samples were collected using Thermosorb/N^{R} adsorption media purchased from Thermo Electron Corporation, Waltham MA, with P200, P200A, P2500, and P2500A DuPont pumps at flow rates of .2 to 2.0 Lpm. Samples were analyzed by the National Institute for Occupational Safety and Health (NIOSH), Cincinnati OH. The adsorption media was desorbed with methanol and dichloromethane (25%/75%) and analyses were accomplished by gas chromatography with detection of NDMA by a Thermal Energy Analyzer (TEA). Presence of NDMA was confirmed by gas chromatography/mass spectroscopy (GC/MS).

III. EXPOSURE STANDARDS

The following standards apply to this survey.

A. Hydrazine

AFOSH Standard 161-13, Hydrazine[3], establishes the permissible exposure limit (PEL) of .1 mg/m³ (100 µg/m³). Hydrazine is also an industrial substance suspect of carcinogenic potential for man and skin absorption can be a significant route of exposure.[1]

B. UDMH

The current American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Values (TLV®) are incorporated into AFOSH Standard 161-8, Permissible Exposure Limits for Chemical Substances.[4] UDMH has an assigned TLV of 1.0 mg/m³ (1000 µg/m³) and also has "skin" and A2 notations,[1] indicating UDMH is an industrial substance suspect of carcinogenic potential for man and skin absorption can be a significant route of exposure.

C. NDMA

NDMA produces tumors in laboratory animals and is covered by AFOSH Standard 161-3, Carcinogenic Substances[2] and 29 CFR 1910.1016, N-nitrosodimethylamine.[5] These regulations specifically apply to mixtures which contain greater than 1% NDMA by weight in the solid or liquid. USAF UDMH and 50/50 mixture analyzed to date contained significantly less than 1% NDMA. However, NDMA may be formed by oxidation of UDMH in air, and due to its potent animal carcinogenicity, human exposures must be lowered as much as possible. NDMA does not have an assigned TLV but does have "skin" and A2 notations.[1]

IV. RESULTS AND DISCUSSION

A. General

Sample results are presented in Tables A-I through A-V in Appendix A. The NPT CONC column in the tables is the concentration in micrograms per cubic meter measured during the sample period adjusted to 25°C, 760 mm Hg (normal pressure and temperature). The TWA CONC column is the concentration time-weighted over 8 hours adjusted to 25°C, 760 mm Hg, assuming no exposure for the unsampled period. Comparisons with previous download surveys are based upon the NPT rather than TWA concentrations to eliminate sampling duration differences. The results with < symbols associated with nondetected (ND) samples indicate the minimum concentration which could have been measured under the sampled conditions.

B. Background Levels

The complexes and dates sampling was performed are presented in Table I and the sample results are summarized in Table II.

TABLE I

Sample Dates

Site	Date
570-1	15 Feb 83
570-4	8 Apr 83
570-6	27 Jan 83
571-4	26 Jan 83
571-9	4 Nov 82

1. Hydrazine and UDMH

Hydrazine and UDMH levels measured did not exceed 1% and 10% 8-hour PEL levels respectively. However, many of the UDMH values could be false positives associated with the analytical method.

2. NDMA

NDMA was detected at the silo exhaust at four complexes with an average concentration of 0.62 µg/m³ (0.20 ppb) for all five complexes measured. It was also detected at the "W" and the MSA platform at two complexes at average concentrations of 0.30 µg/m³ (0.10 ppb) and 0.18 µg/m³ (0.06 ppb) respectively for all complexes measured. NDMA was also detected at complex 570-1 on the P-5 platform at a concentration of 0.24 µg/m³ (0.08 ppb) and in the launch duct on Level 8 and the equipment area on Level 2 of complex 571-9 at levels of 0.35 µg/m³ (0.12 ppb) and 0.12 µg/m³ (0.04 ppb) respectively.

V. CONCLUSIONS

A. UDMH and hydrazine are not significant health hazards based upon current exposure standards.

B. NDMA was not detected in the LCC.

C. NDMA, while present at some locations in the silo area at sub parts per billion concentrations, is not a significant health hazard due to the low levels measured and the limited time spent in the silo by crewmembers (less than 2 hr/alert). This was further confirmed by the lack of NDMA detected on personal samplers worn by crewmembers.

VI. RECOMMENDATIONS

A. Inform missile crewmembers of the presence of NDMA and possible health hazards similar to information briefed to Propellant Transfer System (PTS) personnel.

TABLE II

Sample Result Summary, NPT Conc., µg/m³, Hydrazine/UDMH/NDMA

	570-1	570-4	570-6	571-4	571-9	Average
LCC	<0.7/58/<0.06	<0.6/7.7/<0.05	<0.6/103/	<0.6/91/<0.05	/ /<0.07	<0.6/65/<0.06
Blast Lock 201	<0.8/<9.6/<0.07	<0.6/9.7/<0.05	<0.7/30/<0.06	<0.6/34/<0.05	/ /<0.09	<0.7/<21/<0.06
Silo Exhaust	<0.6/<7.1/<0.05	<0.6/3.9/0.81	<0.7/206/0.73	/ /0.92	1.2/<6.9/0.61	<0.8/<56/<0.62
Level 2, Launch Duct					<0.5/<6.1/<0.09	<0.5/<6.1/<0.09
Level 2, Equipment Area					/ /0.12	/ /0.12
Level 5, Launch Duct					<0.6/<7.1/<0.1	<0.6/<7.1/<0.1
Level 5, Equipment Area					<0.6/<7.3/<0.1	<0.6/<7.3/<0.1
Level 8, Launch Duct					1.2/<7.3/0.35	1.2/<7.3/0.35
Level 8, Equipment Area					1.2/<6.2/<0.10	1.2/<6/<0.10
"W"	<0.7/29/<0.06	<0.6/7.4/<0.05	<0.8/39/0.37	<0.7/81/0.72		<0.7/39/<0.30
Level 9, P-5 Platform	<0.9/77/0.24	<0.6/19/<0.05	/ /<0.06	<0.7/40/<0.06		<0.7/45/<0.10
Level 6, MSA Platform	<0.8/58/<0.07	<0.5/9.4/0.32	<0.7/150/0.27	<0.7/36/<0.06		<0.7/63/<0.18
LCC Personnel	/ /<1.41	/ /	/ /<0.10	/ /<2.24		/<1.25
Average*	<0.8/<40/<.09	<0.6/9.5/<0.22	<0.7/106/<0.30	<0.7/56/<0.31	<0.9/<6.8/<0.18	

*LCC personnel samples were not included in the averages.

References

1. American Conference of Governmental Industrial Hygienists. (1982) TLVs[R], Threshold Limit Values for Chemical Substances and Physical Agents in the Workplace Environment with Intended Changes for 1982. ACGIH, Cincinnati OH.

2. AFOSH Standard 161-3, Carcinogenic Substances, 20 Jun 1977.

3. AFOSH Standard 161-13, Occupational Health Exposure to Hydazine, 26 Dec 79.

4. AFOSH Standard 161-8, Permissible Exposure Limits for Chemical Substances, 20 Jun 78.

5. Code of Federal Regulations, 29 CFR 1910, Nitrosodimethylamine.

APPENDIX A

TABLE A-I

11/4/82, Site 571-9, Background Samples Before Fuel Propellant Download

SAMPLED FOR:

COMPONENT NAME	PEL, µg/m³	LOD, µg	MOLE WT
HYDRAZINE	100.0	.300	32.0
UDMH	1000.0	3.600	60.1
NDMA	NONE ASSIGNED	0.05	74.1

LOCATION	ECH ID#	DUR, min	CHEM NAME	QUANT, µg	NPT CONC, µg/m³	TWA CONC, µg/m³	% PEL	TWA CONC, ppb
LCC	SX822301	397.	Hydrazine	ND*	---	---	---	---
			UDMH	ND*	---	---	---	---
	SX822303		NDMA	ND	<0.07	<0.06	NA	<0.02
Blast Lock, Area 201	SX822321	387.	Hydrazine	**	---	---	---	---
			UDMH	**	---	---	---	---
	SX822323		NDMA	0.063	0.09	0.07	NA	0.02
Level 2, Launch Duct	SX822331	320.	Hydrazine	ND	<0.5	<0.3	0	<0.3
			UDMH	ND	<6.1	<4.1	0	<1.7
	SX822333		NDMA	ND	<0.09	<0.06	NA	<0.02
Level 2, Equipment Area	SX822311	322.	Hydrazine	ND*	---	---	---	---
			UDMH	ND*	---	---	---	---
	SX822313		NDMA	0.071	0.12	0.08	NA	0.03
Level 5, Launch Duct	SX822351	276.	Hydrazine	ND	<0.6	<0.3	0	<0.3
			UDMH	ND	<7.1	<4.1	0	<1.7
	SX822353		NDMA	ND	<0.10	<0.06	NA	<0.02

TABLE A-I Continued

LOCATION	ECH ID#	DUR, min	CHEM NAME	QUANT, µg	NPT CONC, µg/m³	TWA CONC, µg/m³	% PEL	TWA CONC, ppb
Level 5, Equipment Area	SX822341	268.	Hydrazine	ND	<0.6	<0.3	0	<0.3
			UDMH	ND	<7.3	<4.1	0	<1.7
	SX822343		NDMA	ND	<0.10	<0.06	NA	<0.02
Level 8, Launch Duct	SX822371	268.	Hydrazine	0.6	1.2	0.7	1	0.5
			UDMH	ND	<7.3	<4.1	0	<1.7
	SX822373		NDMA	0.17	0.35	0.19	NA	0.06
Level 8, Equipment Area	SX822361	268.	Hydrazine	0.6	1.2	0.7	1	0.5
			UDMH	3.00	6.2	3.4	0	1.4
	SX822363		NDMA	ND	<0.10	<0.06	NA	<0.02
Silo Exhaust	SX822381	297.	Hydrazine	0.6	1.2	0.7	1	0.6
			UDMH	ND	<6.9	<4.3	0	<1.7
	SX822383		NDMA	0.323	0.60	0.38	NA	0.12

* Pump failed
** Samples lost

TABLE A-II

4/8/83, Site 570-4, Background Samples Before Fuel Propellant Download

SAMPLED FOR:

COMPONENT NAME	PEL, µg/m³	LOD, µg	MOLE WT
HYDRAZINE	100.0	.300	32.0
UDMH	1000.0	3.600	60.1
NDMA	NONE ASSIGNED	0.025	74.1

LOCATION	ECH ID#	DUR, min	CHEM NAME	QUANT, µg	NPT CONC, µg/m³	TWA CONC, µg/m³	% PEL	TWA CONC, ppb
LCC Personnel	SX831502	60	NDMA	*	---	---	---	---
Silo Exhaust Shaft	SX831491	291	Hydrazine	ND	<0.6	<0.4	0	<0.4
			UDMH	2.0	3.9	2.4	0	1.0
	SX831492		NDMA	0.430	0.81	0.49	NA	0.16
Launch Control Center	SX831481	292	Hydrazine	ND	<0.6	<0.4	0	<0.3
			UDMH	4.0	7.7	4.7	0	1.9
	SX831482		NDMA	ND	<0.05	<0.03	NA	<0.01
Sump P-5 Platform	SX831471	295	Hydrazine	ND	<0.6	<0.3	0	<0.3
			UDMH	10.0**	19.0	11.4	1	4.6
	SX831472		NDMA	ND	<0.05	<0.03	NA	<0.01
Top of "W" Flame Detector	SX831461	294	Hydrazine	ND	<0.6	<0.3	0	<0.3
			UDMH	4.0	7.4	4.5	0	1.9
	SX831462		NDMA	ND	<0.05	<0.03	NA	<0.01

*Sample lost
**Possible interference from firebrick

TABLE A-II Continued

LOCATION	ECH ID#	DUR, min	CHEM NAME	QUANT, µg	NPT CONC, µg/m³	TWA CONC, µg/m³	% PEL	TWA CONC, ppb
Level 6 MSA Platform	SX831451	301	Hydrazine	ND	<0.5	<0.3	0	<0.3
			UDMH	5.2	9.4	5.9	1	2.4
	SX831452		NDMA	0.173	0.32	0.20	NA	0.07
Blast Lock Area 201	SX831441	301	Hydrazine	0.3	0.6	0.4	0	0.3
			UDMH	5.2	9.7	6.1	1	2.5
	SX831442		NDMA	ND	<0.05	<0.03	NA	<0.01

* Sample lost in analysis

TABLE A-III

1/27/83, Site 570-6, Background Samples Before Fuel Propellant Download

SAMPLED FOR:

COMPONENT NAME	PEL, µg/m³	LOD, µg	MOLE WT
HYDRAZINE	100.0	0.3	32.0
UDMH	1000.0	3.6	60.1
NDMA	NONE ASSIGNED	0.025	74.1

LOCATION	ECH ID#	DUR, min	CHEM NAME	QUANT, µg	NPT CONC, µg/m³	TWA CONC, µg/m³	% PEL	TWA CONC, ppb
LCC	SZ830011	262	Hydrazine	ND	<0.4	<0.3	0	<0.3
			UDMH	49.5	103	56.0	6	23.0
Blast Lock 201	SX830021	241	Hydrazine	ND	<0.7	<0.3	0	<0.3
			UDMH	13.2	30.0	15.0	2	6.1
	SX830023		NDMA	ND	<0.06	<0.03	NA	<0.01
Level 6 MSA Platform	SX830031	236	Hydrazine	ND	<0.7	<0.3	0	<0.3
			UDMH	66.	152.	75.0	7	30.0
	SX830033		NDMA	0.118	0.27	0.13	NA	0.04
Top of "W"	SX830041	229	Hydrazine	ND	<0.8	<0.4	0	<0.3
			UDMH	15.4	39.0	18.0	2	7.5
	SX830043		NDMA	0.156	0.37	0.18	NA	0.06
Level 9 on P-5 Platform	SX830051	*	Hydrazine	ND	----	----	----	----
		*	UDMH	15.4	----	----	----	----
	SX830053	225	NDMA	ND	<0.06	<0.03	NA	<0.01

* Pump failed

TABLE A-III Continued

LOCATION	ECH ID#	DUR, min	CHEM NAME	QUANT, µg	NPT CONC, µg/m³	TWA CONC, µg/m³	% PEL	TWA CONC, ppb
Silo Air Exhaust Grill	SX830061	228	Hydrazine	ND	<0.7	<0.3	0	<0.3
			UDMH	85.8	206	98.0	10	40.0
	SX830063		NDMA	0.305	0.73	0.35	NA	0.12
LCC Personnel	SZ830013	1388	NDMA	ND	<0.10	<0.10	NA	<0.03

* Pump failed

TABLE A-IV

1/26/83, Site 571-4, Background Samples Before Fuel Propellant Download

SAMPLED FOR:

COMPONENT NAME	PEL, µg/m³	LOD, µg	MOLE WT
HYDRAZINE	100.0	0.3	32.0
UDMH	1000.0	3.6	60.1
NDMA	NONE ASSIGNED	0.025	74.1

LOCATION	ECH ID#	DUR, min	CHEM NAME	QUANT, µg	NPT CONC, µg/m³	TWA CONC, µg/m³	% PEL	TWA CONC, ppb
LCC	SX830081	280	Hydrazine	ND	<0.6	<0.3	0	<0.3
			UDMH	46.2	91.0	53.0	5	22.0
	SX830083		NDMA	ND	<0.05	<0.03	NA	<0.01
Midway in "W"	SX830091	240	Hydrazine	ND	<0.7	<0.3	0	<0.3
			UDMH	36.3	81.0	41.0	4	17.0
	SX830093		NDMA	0.319	0.72	0.36	NA	0.12
Level 9 on P-5 Platform	SX830101	235	Hydrazine	ND	<0.7	<0.3	0	<0.3
			UDMH	17.6	40.0	20.0	2	8.0
	SX830103		NDMA	ND	<0.6	<0.03	NA	<0.01
Level 6 MSA Platform	SX830111	229	Hydrazine	ND	<0.7	<0.3	0	<0.3
			UDMH	15.4	36.0	17.0	2	7.0
	SX830113		NDMA	ND	<0.06	<0.03	NA	<0.01
Blast Lock 201	SX830131	270	Hydrazine	ND	<0.6	<0.3	0	<0.3
			UDMH	16.5	34.0	19.0	2	8.0
	SX830133		NDMA	ND	<0.05	<0.03	NA	<0.01

TABLE A-IV Continued

LOCATION	ECH ID#	DUR, min	CHEM NAME	QUANT, µg	NPT CONC, µg/m³	TWA CONC, µg/m³	% PEL	TWA CONC, ppb
Silo Exhaust	SX830121	231	Hydrazine	*	----	----	----	----
			UDMH	*	----	----	----	----
	SX830123		NDMA	0.389	0.92	0.44	NA	0.15
LCC Personnel	SZ830073	60	NDMA	ND	<2.24	<0.28	NA	<0.09

* Sample not received by USAF OEHL

TABLE A-V

2/15/83, Site 570-1, Background Samples Before Fuel Propellant Download

SAMPLED FOR:

COMPONENT NAME	PEL, µg/m³	LOD, µg	MOLE WT
HYDRAZINE	100.0	0.3	32.0
UDMH	1000.0	3.6	60.1
NDMA	NONE ASSIGNED	0.025	74.1

LOCATION	ECH ID#	DUR, min	CHEM NAME	QUANT, µg	NPT CONC, µg/m³	TWA CONC, µg/m³	% PEL	TWA CONC, ppb
LCC	SX830141	249	Hydrazine	ND	<0.7	<0.3	0	<0.3
			UDMH	26.4	58.2	30.2	3	12.3
	SX830143		NDMA	ND	<0.06	<0.03	NA	<0.01
Blast Lock 201	SX830151	205	Hydrazine	ND	<0.8	<0.3	0	<0.3
			UDMH	ND	<9.6	<4.1	0	<1.7
	SX830153		NDMA	ND	<0.07	<0.03	NA	<0.01
Level 6	SX830161	195	Hydrazine	ND	<0.8	<0.3	0	<0.3
			UDMH	20.9	58.4	23.7	2	9.6
	SX830163		NDMA	ND	<0.07	<0.03	NA	<0.01
Top of W	SX830171	247	Hydrazine	ND	<0.7	<0.3	0	<0.3
			UDMH	13.2	29.1	15.0	1	6.1
	SX830173		NDMA	ND	<0.06	<0.03	NA	<0.01
Level 9, P-5 Platform	SX830181	178	Hydrazine	ND	<0.9	<0.3	0	<0.3
			UDMH	25.3	77.4	28.7	3	11.7
	SX830183		NDMA	0.08	0.24	0.09	NA	0.03

TABLE V Continued

LOCATION	ECH ID#	DUR, min	CHEM NAME	QUANT, µg	NPT CONC, µg/m³	TWA CONC, µg/m³	% PEL	TWA CONC, ppb
Silo Exhaust	SX830191	277	Hydrazine	ND	<0.6	<0.3	0	<0.3
			UDMH	ND	<7.1	<4.1	0	<1.7
	SX830193		NDMA	ND	<0.05	<0.03	NA	<0.01
LCC Personnel	SZ830203	100	NDMA	ND	<1.41	<0.29	NA	<0.20 <0.10

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